Analysis of Ambient Hydroperoxides in Pellston Michigan, July 2001

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Abstract

Hydroperoxides (H_2O_2 and ROOH) in atmospheric chemistry are very important for the study of air pollution. These peroxides are participants in the chemical reactions that form ozone. Peroxides degrade air quality, form acid rain and also may damage trees because they damage plant cells and therefore might contribute to the decline of forests (Sakugawa et.al., 1990). Some researchers believe that the reaction of ozone with terpenes and isoprene emitted by plants produce a variety of radicals that contribute to the formation of hydroperoxides. Hydroperoxides were determined during the field experiment in the University of Michigan Biological Station (UMBS) **P**rogram for **R**esearch on **O**xidants:

Abstract (Cont.)

PHotochemistry, **E**missions, and **T**ransport (PROPHET), at the top of a 30m tower, near Pellston MI in July 2001. PROPHET was established at the UMBS to help us to understand interactions between sunlight, nitrogen oxides, and volatile organic compounds that result in the formation of ozone and other oxidants. Hydroperoxides were collected using an aqueous coil scrubber fitted with an “inletless” inlet to avoid peroxide loss during collection. Samples were subsequently analyzed by fluorescence detection. Our results show that this method has potential to detect peroxides at an unattended site outdoors.

Introduction

In recent years, scientists have tried to develop different methods to study the hydroperoxides (ROOH and H_2O_2) in the atmosphere. These peroxides play an important role in atmospheric chemistry reactions. To understand the peroxide, is important to know the reactions that are involved, both in its formation and its loss reactions. Peroxides are produced through a series of gas-phase free-radical reactions initiated by the photolysis of O_3 to form O radical, which produces hydroxyl radicals (OH) upon reaction with water. Hydroxyl radicals then react with hydrocarbons and/or CO, ultimately to produce HO_2 and RO_2 radicals, which disproportionate to give H_2O_2 and

Introduction (Cont.)

ROOH and O_2 (Lee et.al.,1994). Table 1 shows these gas phase reactions.

Because both HO_2 and H_2O_2 are water soluble, there are similar reactions that occur in cloud, rain and fog droplets. In urban air, anthropogenic hydrocarbons react rapidly with OH to form ozone. However, in rural and forested environments, biogenic hydrocarbons, like isoprene and terpenes, are most reactive with OH.

My experiment was to evaluate a new autosampler-based method for peroxide analysis in the laboratory and during a field experiment with the PROPHET program in Pellston, MI

Introduction (Cont.)

in July 2001. PROPHET has different objectives: (1) obtain data of the climatology of ozone, ozone precursors and products of photochemical photooxidation, (2) to determine the photochemical and transport processes responsible for the formation and loss of ozone and (3) to identify the role midwest sources play in the transport of pollutants to the northeastern United States and to Canada. We used fluorescence to detect peroxides.

The proposed peroxide measurement generated data on both H_2O_2 and organic peroxide ROOH because ROOH is likely to be a significant fraction of the peroxides in rural/forested environments.

Introduction (Cont.)

Table 1. Sources of atmospheric hydroperoxides

Reactions
(1) $O_3 \xrightarrow{h\nu} O(^1D) + O_2$
(2) $O(^1D) + H_2O \longrightarrow 2OH$
(3) $OH + CO \xrightarrow{O_2} HO_2 + CO_2$
(4) $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$
(5) $HO_2 + RO_2 \longrightarrow ROOH + O_2$

Instrumentation

- Model FL-750BX HPLC McPherson Fluorescence Detector
  - Highly sensitive 0.1 pg until 05 pg.
  - Continuously variable excitation wavelength.
  - Compatible with all liquid chromatographs.

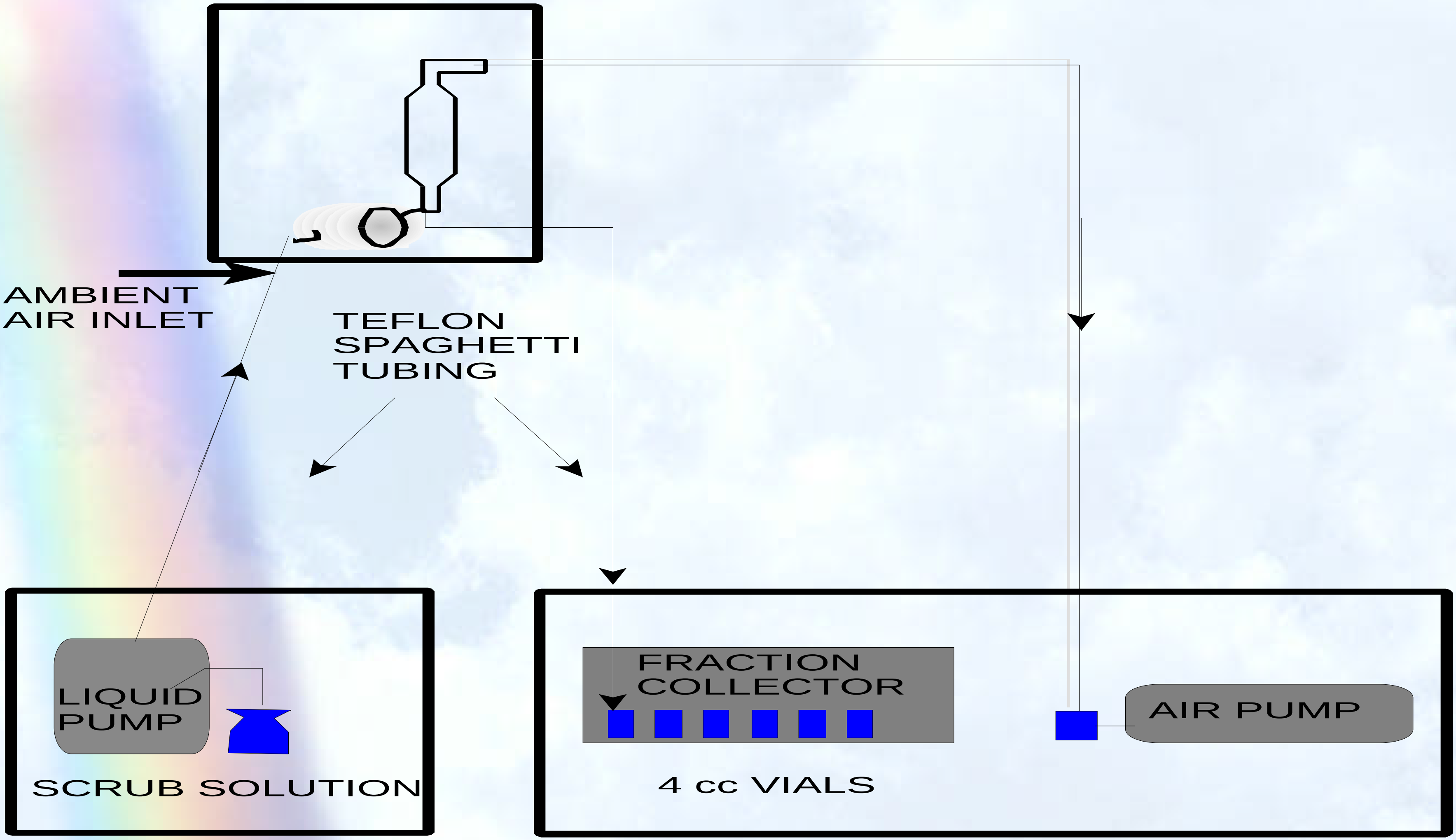
Instrumentation (Cont.)

- CS-9000 Random Access Sampler
  - Reliability
  - Simplicity
  - Versatility
  - Sampling for a wide variety of analytical systems, including:
    - Continuous Flow Analyzers
    - ICP
    - HPLC
    - Atomic Absorbtion and other analytical instruments

Analytical Method

- **Instrument:**
  - We used a coil scrubber to collect peroxide from air and dissolve it in scrubbing solution. This solution was delivered by a peristaltic pump into vials for subsequent analysis using a Westco autosampler.
  - We mounted the instrument at the top of a 30m tower.
  - It ran unattended for 14 hour periods typically, with 15 minute sampling time.
  - Vials were analyzed by fluorescence detection using a McPherson model 750 detector set at λ_{ex}=305nm for FeBA and 320nm for pOHPAA.
  - Data was collected using LABTECH NOTEBOOK.

Schematic Diagrams



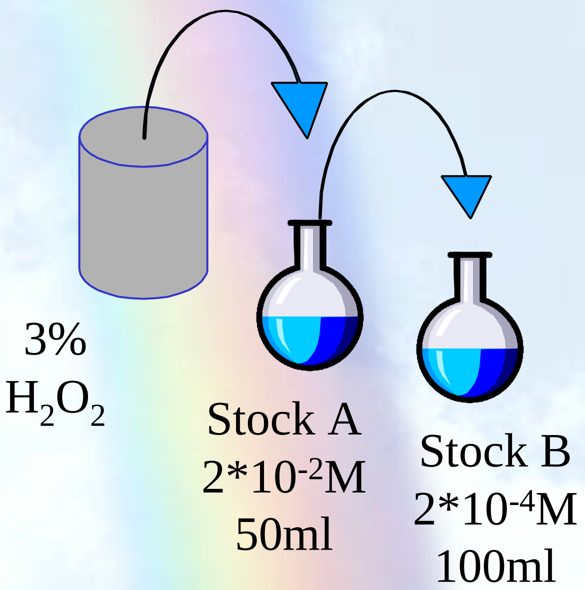
Top of Instrument Tower

Analytical Method (Cont.)

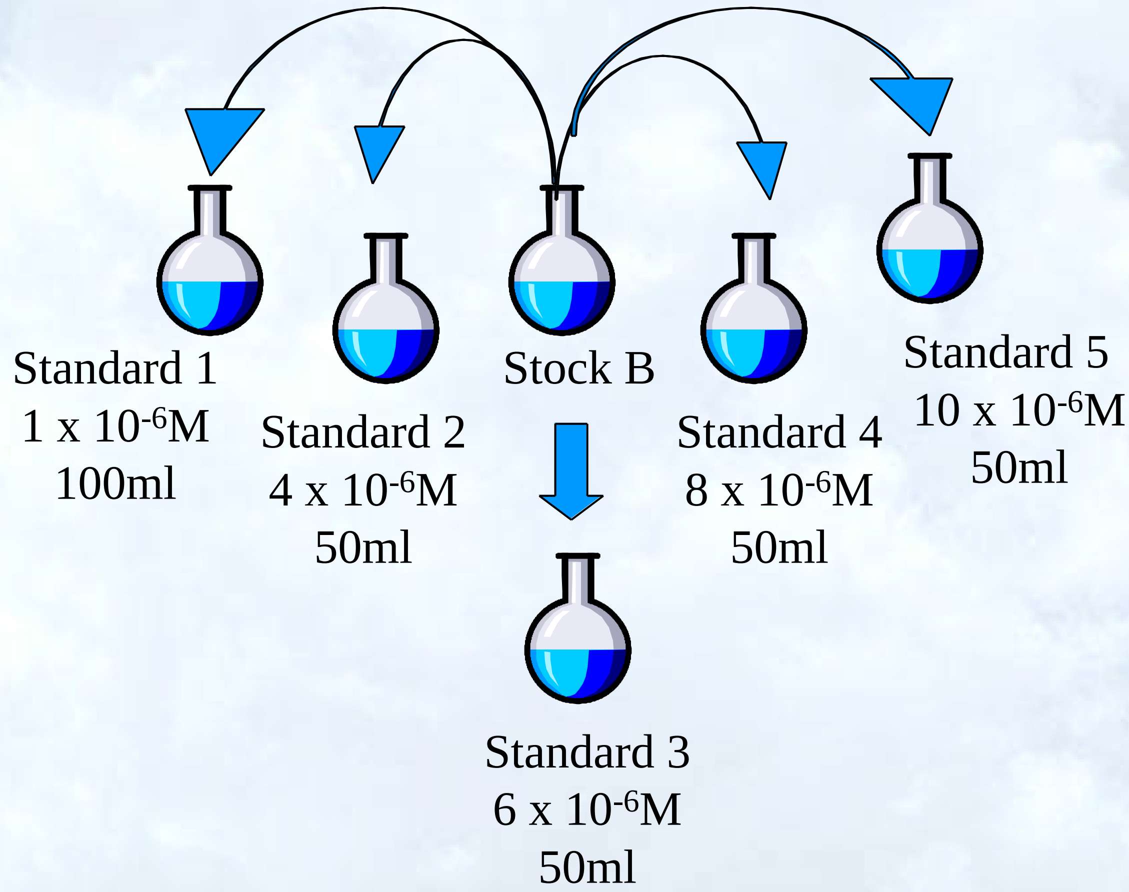
- **Reagents:**
  - Vials were prefilled with 2ml of *FeBA or **pOHPAA before scrubbed air samples were added.
  - FeBA (Benzoic acid, H_2SO_4 and $FeSO_4$)
  - pOHPAA/HRP (TRIS base, pOHPAA, HCl and HRP solid)
  - Each batch of vials was accompanied by a set of H_2O_2 standards prepared by serial dilution of 3% H_2O_2. This concentration of H_2O_2 in this solution was determined by titration. (See Figure)

Preparation of Stock and Standards Solutions

Step 1

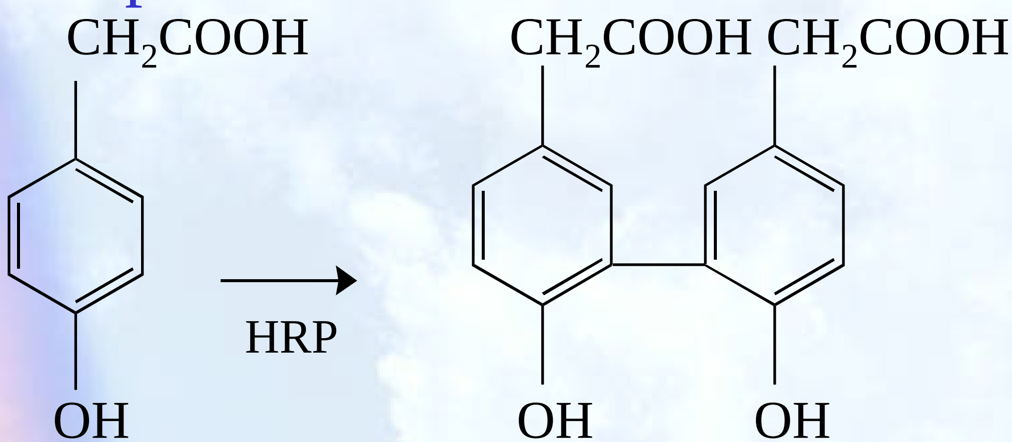


Step 2



Reactions Involved

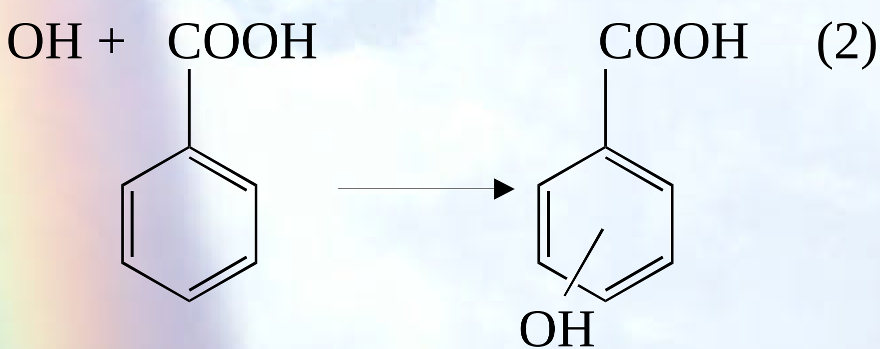
**pOHPAA Reaction



Dimer+NaOH
enhances fluorescence
λ_{ex} =320nm

*FeBA Reaction

$$Fe\ (II) + H_2O_2 \longrightarrow OH + OH^- + Fe\ (III) \quad (1)$$



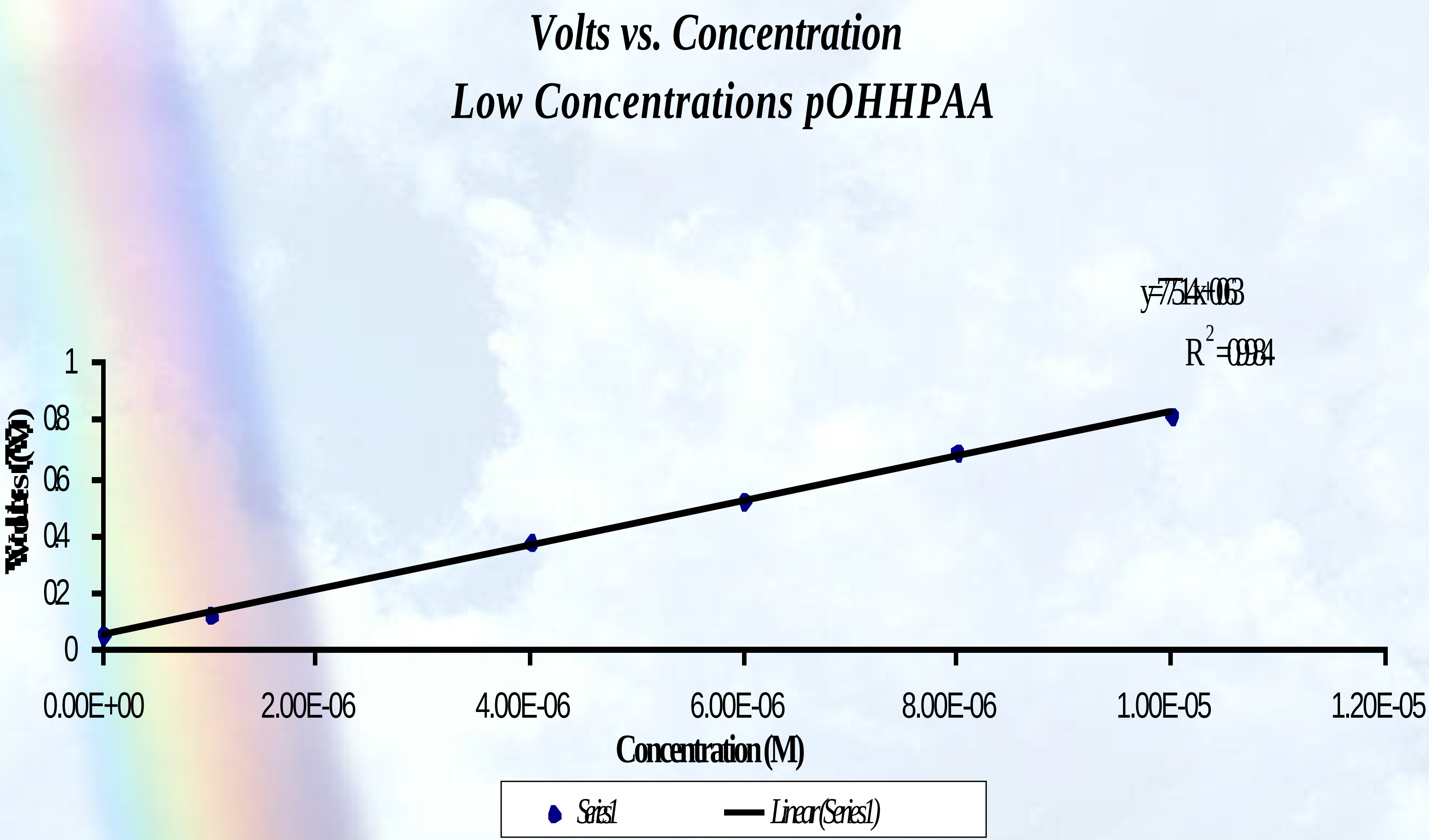
Al (III) + BA
↓
Al-BA
enhances fluorescence
λ_{ex} =305nm

Instrument Test

We carried out experiments in the laboratory to characterize the instrument.

- **Is the instrument linear?**
  - Yes- We delivered a series of aqueous peroxide standards to a series of vials. (See Calibration Curve)
- **Is the measurement technique reproducible?**
  - Yes, we delivered an aqueous H_2O_2 standard to a series of 10 vials, prefilled with *FeBA and **pOHPAA and then we read the fluorescence. The results were 2.00 $\pm$ .04 and 2.00 $\pm$ .01 μM respectively.

Calibration Curve Graph

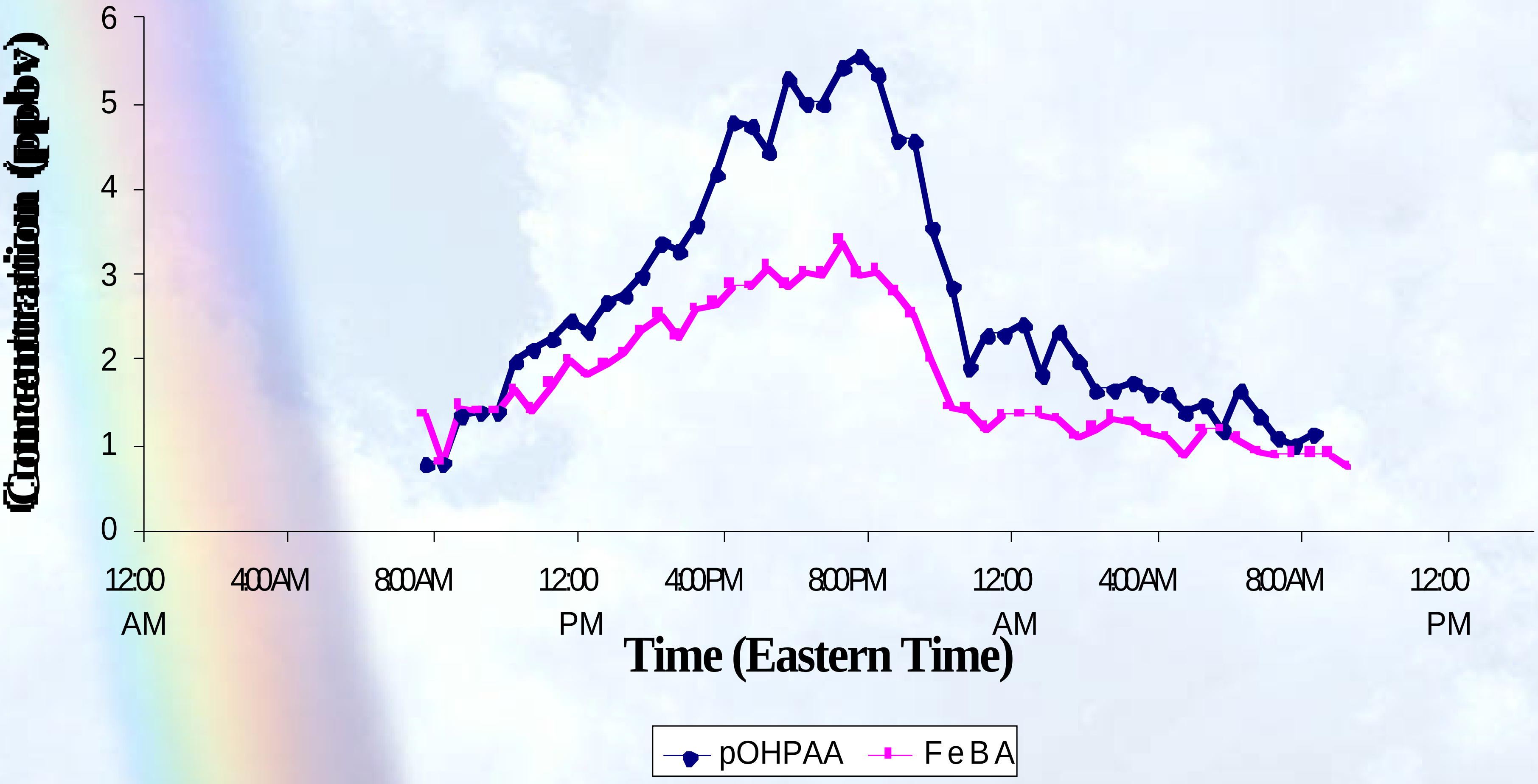


Instrument Test (Cont.)

- **Does the peroxide decompose in metal needle?**
  - Metals are known to decompose peroxides, and the autosampler used a stainless steel needle to pierce the covers. We collected an aqueous peroxide standard in a series of 10 vials with and without the metal needle. The results were 2.00 $\pm$ 0.02 μM with the needle and 2.00 $\pm$ 0.03 μM without the needle. Therefore, the samples are not decomposed by the needle.

Data Analysis

Peroxides at Pellston, MI on July 8-9, 2001



Conclusion

During this summer I became familiar with the literature about peroxides and how they contribute to the formation of ozone in ambient air. The instrumentation and the techniques to measure hydroperoxides worked very well. Preliminary data from Pellston, MI is presented. Higher concentrations of hydroperoxides predominate during the afternoon when sun is strongest and lowest concentrations at night. We can see the difference between pOHPAA and FeBA, pOHPAA is higher because responds to all peroxides and FeBA responds only H_2O_2.

Future Work

The next step will be to perform continuous tests on the instrument. Some of the questions we need to answer are: (1) Is the measurement technique reproducible with a gas-phase peroxide standard? (2) How well does this system discriminate between H_2O_2 and ROOH? (3) Is there SO_2 and O_3 interference?

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